



Membrane stability studies for vanadium redox cell applications

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Abstract

Accelerated degradation tests of selected membranes were carried out to determine their stability in the fully charged positive electrolyte solution of the vanadium redox battery. Each membrane was soaked in both 1.0 and 0.1 M V(V) solutions for extended periods of time and UV–visible spectroscopy was used to determine the rate of oxidation of the membrane by V(V) to produce V(IV) ions in solution. The membranes were then evaluated for any changes in their resistance, IEC, diffusivity and water transfer properties. FESEM was used to analyse the membranes for physical damage. Different trends were observed in the 1.0 and 0.1 M V(V) electrolytes. Of the membranes studied, Nafion 112E/H⁺ showed the worst stability in the 0.1 M V(V) solution but one of the best stabilities in 1.0 M V(V). The dilute V(V) electrolyte appears to enter the pores of the membrane more readily as the membranes swell significantly in this solution. The 0.1 M V(V) solution therefore causes accelerated deterioration of the membrane performance as a result of physical destruction, chemical modification or a combination of both. The effect is more pronounced in the membranes that have a higher degree of swelling in the vanadium electrolyte.

1. Introduction

For a membrane to be suitable for a particular application, it must be stable in the medium and maintain its properties over long periods of exposure. Previous studies by Llewellyn et al. [1] and Mohammadi and Skyllas Kazacos [2] showed that most early types of commercially available membranes tended to deteriorate in the highly oxidising V(V) electrolyte. These membranes were therefore unable to offer long cycle life when used as ion exchange membranes in the vanadium redox battery (VRB) [3–6]. Nafion 112 and 117 membranes showed good chemical stability [2], but these are currently too expensive for commercial use. More recently, however, commercial membranes were developed that show excellent long-term stability [7, 8] in the VRB, but their cost is still high for many applications. An on-going effort is thus required to find suitable commercial membranes that can combine long cycle life, high performance and low cost for the VRB system. It is also of interest to evaluate candidate membranes for the VRB so as to develop guidelines to the selection and development of suitable membranes for the VRB and to gain a better understanding of their behaviour and properties during long-term operation in commercial energy storage systems.

Newer developmental and commercially available membranes were therefore further evaluated for their stability in the vanadium electrolytes. Extended exposure

of the membranes to the vanadium electrolytes could cause physical breakdown of the membrane, de-cross-linking resulting in increased swelling, loss in acidity or basicity as functional groups are replaced, change in total ion exchange capacity (IEC) or poisoning of the functional groups or fouling from precipitation of ions.

A decrease in the conductivity of the membrane during operation will affect the voltage efficiency of the cell, while an increase in diffusion of the vanadium ions would indicate that the membranes are no longer performing efficiently as ion selective membranes. An increase in the rate of diffusion of the vanadium ions across the membrane will lead to an increased self-discharge rate and a loss in coulombic efficiency, which is undesirable.

The selected membranes were evaluated for any change in their resistance, IEC, vanadium ion diffusivity and appearance. Physical damage was evaluated using field emission scanning electron microscopy (FESEM), and continuous charge/discharge cycling of small vanadium test cells were undertaken to determine whether any of these properties had been compromised by extended exposure to the vanadium electrolytes.

2. Experimental

Membranes studied included the cation exchange Gore Select L-570, L-01009, L-01854 and P-03430 (Gore Tex,

USA), in addition to the anion exchange New Selenion Type 3H (Asahi Glass, Japan) as well as a sample anion exchange membrane from Tokuyama (Japan). Their properties were compared against those of Nafion 112E (DuPont), which had been previously shown to possess good stability and performance in the VRB [2].

In this study accelerated degradation of the membranes was carried out by soaking each material in a 0.1 M V(V) solution, which was prepared by diluting the fully charged 2 M vanadium positive half-cell electrolyte. To establish a rate and degree of deterioration a specific area of each membrane (60 × 60 mm) was soaked in the 0.1 M V(V) solution for 60 and 120 days. The IEC and the conductivity of each of the membranes were determined after 60 and 120 days exposure to the 0.1 M V(V) solution. Diffusion tests were also conducted on the treated membranes to determine whether the vanadium ion diffusivity of each membrane had been adversely affected.

FESEM was also used to try to identify any physical damage on the surface of the membranes.

2.1. Diffusivity tests

The permeability of each membrane to the vanadium ions was determined by measuring the static diffusion of the vanadium(IV) ions across the membrane using a static cell as described by Llewellyn et al. [1]. The membrane was pressed between two polyvinyl chloride (PVC) half-cells with rubber gaskets on either side to prevent solution leakage. The cell was held together using a G-clamp. A solution of 1 M VOSO₄ in 2.5 M H₂SO₄ was placed in one half-cell and a solution of 1 M MgSO₄ in 2.5 M H₂SO₄ in the other. The MgSO₄ solution was used to equalise the ionic strengths of the two solutions and to minimise any osmotic pressure effects. The membrane area exposed to the solutions was 25 cm² (5 cm × 5 cm) while the volume of the solutions for each half-cell was 50 ml. Samples of the MgSO₄ solution (initially free from VOSO₄ ions) were taken periodically and the absorbance of the solution measured using an UV-Visible spectrophotometer to evaluate the permeability of the vanadium(IV) ions through the membranes. The sample solution was returned to the cell. The absorbance of the vanadium solution is related to its concentration according to Beer's law. The rate of change in the solution absorbance was used to calculate the diffusion coefficient for the V(IV) ion according to the method described by Llewellyn et al. [1]. Briefly, this method is based on Fick's First Law. For diffusion across a membrane, this can be represented as

$$N_1 = k_s(C_{1,A} - C_{1,B})$$

where N_1 is the flux of species 1 (mol cm⁻² s⁻¹), k_s is the membrane mass transfer coefficient (cm s⁻¹), $C_{1,A}$ and $C_{1,B}$ the concentration of species 1 in solutions A (blank solution) and B (V(IV) solution), respectively (mol cm⁻³).

Combining this with Beer's Law, it is possible to obtain the following relationship [1]:

$$\ln[\text{absB}^0 - 2 \text{absA}] = \ln[\text{absB}^0] - 2k_s A t / V_A$$

where absB^0 is the initial absorbance of solution B (i.e. V(IV) solution), absA , the absorbance of solution A (i.e. MgSO₄ solution), A , the area of membrane, V_A , the volume of solution A.

A plot of $\ln [\text{absB}^0 - 2\text{absA}]$ vs t should therefore give a straight line with slope equal to $2k_s A / V_A$ from which the value of k_s can be determined.

2.2. Area resistance measurements

The area resistance was measured by the method described by Chieng and Skyllas-Kazacos [9]. For the area resistance measurements, the membranes were exposed to a solution of 2 M VOSO₄ in 3 M H₂SO₄ in both half-cells. The test membrane was placed between two rubber gaskets containing a 1 cm diameter hole in the centre and pressed between the two half cells. Silicone rubber was used to glue the membrane to the rubber gaskets to ensure that the membrane area exposed to the solution was the same as the 1 cm diameter hole area cut into the gaskets. Fifty millilitre of the solution was added to each half-cell. Two graphite plates were used as the electrodes. Electrical contact was provided by a copper rod, which was inserted into the graphite plates. The conductometer employed a low voltage high frequency AC signal to ensure no significant reaction took place at the electrodes. A conductance reading was taken when the conductometer displayed a stable value.

To determine the membrane resistance the measurement was repeated with the same set up, but without a membrane. The area resistance of the membrane was calculated using Equation 1 [10].

$$R = \frac{\text{Membrane area} \times 1000}{C} \quad (1)$$

where R is the area resistance of the cell (Ω cm²), C , the conductance of the cell (mS) and membrane area 0.785 cm². The area resistance of the membrane was calculated by subtracting the cell resistance without the membrane from the resistance measured with a membrane.

2.3. Chemical stability study

The following procedure, as described by Chieng [11] and Mohammadi [10], was used to investigate the chemical stability of the membranes. A specific area (5 cm × 8 cm) of the membrane was pre-weighed and soaked in a known volume of 0.1 or 1 M V(V) solution in 5 M total sulphate. Oxidation of the membrane by V(V) ions leads to the formation of the blue V(IV)

species, which may be used as an indicator to measure the stability of a particular membrane. The concentration of the V(IV) ions was determined by UV-visible spectrophotometry. The absorbance of each solution was periodically determined to monitor the rate of oxidation by V(V). To standardise the method, mixtures of 0.1 M V(IV) solution (prepared by the dilution of the fully discharged positive half-cell electrolyte) and 0.1 M V(V) solution were prepared at different ratios. The absorbance was determined for each mixture at a wavelength of 760 nm at which the maximum absorbance of V(IV) ions takes place and a plot of absorbance vs% V(IV) was obtained as shown in Figure 1.

2.4. Ion exchange capacity (IEC) measurements

The IEC of the membranes was determined using a titration method [10, 11]. The fixed ions such as SO_3^- groups were titrated with 0.05 M KOH, while groups like R_4N^+ were titrated with 0.05 M HCl. The membrane in the Na^+ form was soaked in 1 M HCl solution to convert it to the H^+ form membrane. The membrane was then immersed in a known volume of 0.05 M KOH solution for 48 h at room temperature. The amount of H^+ (in millimoles) was determined by back titration with a 0.05 M HCl solution. The membrane in the Cl^- form was soaked in 1 M KOH solution to convert it to the OH^- form membrane. The membrane was then immersed in a known volume of 0.05 M HCl for 48 h at room temperature. The amount of OH^- (in millimoles) was determined by back titration with a 0.05 M KOH solution. The membrane was then washed with distilled water and dried under vacuum. The IEC was calculated as the ratio of the amount of H^+ or OH^- to the weight of the dried membrane.

2.5. Cell cycling experiments

The performance of the membrane in the flow cell is one of the major considerations when selecting a membrane for the vanadium battery. The Gore Select L-570 and L-01009 membranes were exposed to repeated charge/discharge cycles and the battery efficiencies were monitored. The following equations were used to calculate the cell efficiencies:

Coulombic efficiency is the ratio of the coulombs obtained during discharge to the coulombs needed to charge the cell:

$$\eta_c = \frac{I_{\text{disch}} t_{\text{disch}}}{I_{\text{ch}} t_{\text{ch}}}$$

Energy efficiency:

$$\eta_e = \eta_c \times \eta_v = \frac{I_{\text{disch}} V_{\text{disch}} t}{I_{\text{ch}} V_{\text{ch}} t}$$

Voltage efficiency:

$$\eta_v = \eta_e / \eta_c$$

where η_c is the coulombic efficiency, I_{disch} , the discharge current, t_{disch} , the discharge time, I_{ch} , the charge current, t_{ch} , the charge time, η_e , the energy efficiency, η_v , the voltage efficiency, V_{disch} , the average discharge voltage and V_{ch} , the average charge voltage.

The PVC cell used to evaluate the performance of the membranes comprised of two symmetrical half-cells, each employing a graphite felt electrode (25 cm^2) against graphite and copper plate current collectors. The thickness of the graphite felt used was 3 mm, while the thickness of each half-cell cavity was 5 mm. Electrical contact between the felt, graphite plate and copper current collector was provided by compression when the cell was assembled. The test membrane (exposed area 25 cm^2) was placed between two flow frames to separate the two half-cells. Rubber gaskets were used between cell components to provide seals. The cell components were compressed between two PVC plates held together with nuts and bolts. For the charging/discharging cycles the solution in each half-cell consisted of 100 ml of a 2 M vanadium solution comprising 1 M V(III) plus 1 M V(IV) in 5 M total sulphate (referred to as $\text{V}^{3.5+}$). The cell components, reservoirs and pumps were connected using clear polyethylene tubes.

The charge/discharge cycling was performed at a constant current density of 20 mA cm^{-2} using an in-house automatic controller. The cell was charged to an upper limit voltage of 1.8 V and lower voltage limit of 1.0 V.

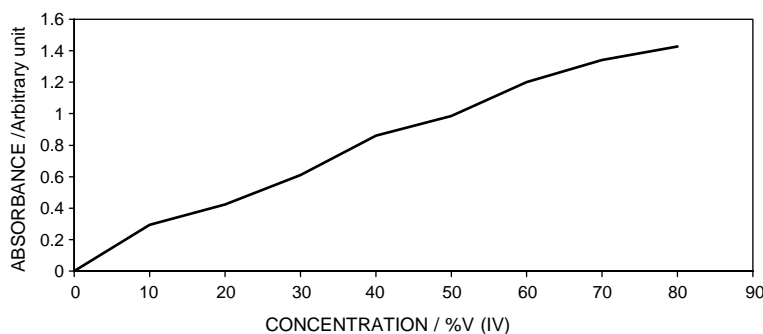


Fig. 1. Absorbance of V(IV)/V(V) solutions at different ratios.

3. Results and discussion

3.1. Diffusion, conductivity and ion exchange capacity

As mentioned previously, it is necessary that the membranes maintain their properties in the vanadium electrolytes to ensure a long cycle life of the VRB. Tests were thus conducted to evaluate the stability of the selected membranes in the vanadium electrolytes. The IEC, resistivity and diffusivity of the membranes was tested after soaking the membranes in a solution of 0.1 M V(V) in 0.25 M H₂SO₄ for 60 and 120 days.

As shown in Tables 1 and 2, the resistivity of each membrane decreases after exposure, while both the IEC and diffusivity of each membrane increase. For example, the resistivity of the Nafion membrane dropped from 2.1 to 0.9 $\Omega \text{ cm}^2$ after being soaked in the vanadium electrolyte for 60 days. Similarly, the resistivity of the Gore Select L-570 membrane dropped from 1.8 to 1.0 $\Omega \text{ cm}^2$. The resistivity of the Gore Select L-01009, L-01854 and P-03430 membranes did not drop as significantly, showing better stability in the vanadium electrolyte. The resistivity of the New Selemion also remained unchanged while the resistivity of the Tokuyama membrane increased, suggesting that it may be fouling in the vanadium electrolyte.

The IEC of every membrane also increased by between 50 and 60% after soaking in the vanadium electrolyte for 60 days and continued to increase with extended soaking. For example, the IEC of the Gore Select L-01009 membrane increased from 1.1 to 2.5.

The rate of vanadium ion diffusion across the membranes did not increase significantly for the Nafion, Gore Select L-570 and L-01009 or the New Selemion. On the other hand, the Gore Select L-01854 and P-03430 membranes show a large increase in their V(IV) ion diffusivities after soaking in the vanadium electrolyte for 60 days. The Tokuyama membrane shows a drop in diffusivity again indicating the membrane may be fouling in the vanadium electrolyte.

The resistivities of the membranes soaked in the vanadium electrolyte for 120 days were similar to those soaked for 60 days. For example, after 60 days of soaking the resistivity of the Nafion dropped to 0.9 $\Omega \text{ cm}^2$, while the resistivity of the L-570 membrane dropped to 1.0 $\Omega \text{ cm}^2$ after soaking for 60 days.

The decrease in resistance of the membranes may be due to the erosion of polymeric material or may be a consequence of the increased IEC and diffusivity. Also, swollen membranes have a higher electric conductivity due to the high content of mobile ions. The membranes did show a high level of swelling in the 0.1 M V(V) solutions. The increase in the IEC of each membrane may be due to SO_4^{2-} or HSO_4^- ions lodging in the pores of the membranes and acting as co-ions in the case of the cation exchange membranes. If the negative ions such as SO_4^{2-} or HSO_4^- lodged into the pores of the membrane, this would increase the flow of hydrogen ions and improve the conductivity of the membrane.

As the permeability of the membrane increases the selectivity decreases. Initially it was thought that this may be a result of ions in the electrolyte forming neutral

Table 1. Stability of membranes soaked in 0.1 M V(V) electrolyte for 60 days

Membrane	Resistivity / $\Omega \text{ cm}^2$		IEC /mmol g ⁻¹		V(IV) Diffusivity / $10^{-3} \text{ cm}^2 \text{ min}^{-1}$	
	Initial	Final	Initial	Final	Initial	Final
Cationic						
Nafion 112E/H ⁺	2.1	0.9	1.5	2.3	1.34	1.64
Gore Select L-570	1.8	1.0	2.0	3.1	1.31	1.34
Gore Select L-01009	1.4	1.1	1.1	2.0	0.92	1.06
Gore Select L-01854	1.2	0.9	2.6	4.1	0.16	0.44
Gore Select P-03430	1.8	1.3	7.9	12.4	0.68	3.30
Anionic						
New Selemion Type 3H	0.9	0.9	2.0	3.0	8.00E-05	8.00E-05
Tokuyama	1.9	2.6	8.8	13.7	0.29	0.054

Table 2. Stability of membranes soaked in 0.1 M V(V) electrolyte for 120 days

Membrane	Resistivity / $\Omega \text{ cm}^2$		IEC /mmol g ⁻¹		V(IV) Diffusivity / $10^{-3} \text{ cm}^2 \text{ min}^{-1}$	
	Initial	Final	Initial	Final	Initial	Final
Nafion 112E/H ⁺	2.1	0.9	1.5	3.6	1.34	4.52
Gore Select L-570	1.8	1.1	2.0	5.2	1.31	2.30
Gore Select L-01009	1.4	1.0	1.1	2.5	0.92	0.98
Gore Select L-790	1.3	0.9	8.1	17.6	8.70E-01	–

complexes with the counter ions present in the pores of the membrane rendering the membranes neutral, therefore reducing their ability to control the flow of ions and increasing level of diffusion of V(IV) ions. Yet, an increase in IEC is observed. After soaking the cation exchange membranes for 60 days, the Nafion 112E/H⁺ and L-01854 membranes displayed the lowest resistivities followed by the Gore Select L-570, L-01009 and P-03430 membranes. Yet, the P-03430 membrane displayed one of the highest ion exchange capacities after soaking for 60 days followed by L-01009, Nafion L-570, L-01854 and finally the P-03430 membrane. The L-01854 membrane also had the highest diffusivity with exposure to the vanadium solution followed by L-01009, L-570, Nafion and the P-03430 membrane. Again the membranes with the higher IEC did not necessarily have the lowest diffusivity or lowest resistance.

The anionic New Selemion Type 3H and Tokuyama membranes, displayed an increase in resistance and a slight increase in IEC, but the New Selemion Type 3H maintains its ion diffusivity properties. Furthermore, the Tokuyama membrane displays an increase in IEC and decrease in the rate of ion diffusion. This may be due to V(V) ions lodging in the pores of the membrane which causes the membrane to take on a yellow colour. The increase in resistance of the membranes and the decrease in rate of ion diffusion across the Tokuyama membrane may thus be a result of fouling. The change in resistance of the membranes tends to occur within the first 60 days of exposure to the vanadium electrolyte, while the IEC and diffusivity of the membranes continue to change with exposure. Due to the significant rate at which the IEC of the membranes increases it may be assumed that ions such as SO₄²⁻ or HSO₄⁻ are lodging in the pores of the membrane and acting as co-ions. This also explains the increase in the rate of diffusion of positive vanadium ions.

The change in the membrane properties may be due to the polymer material degrading in the oxidising vanadium(V) solution. The membranes should lose weight as the polymer material degrades. To investigate this theory the membranes were exposed to the 0.1 M V(V) solution in 0.25 M H₂SO₄ for 500 days. The membranes were subsequently soaked in distilled water for 24 h and vacuum dried before being weighed. The weight of the membranes was checked before and after exposure to the electrolyte. As shown in Table 3 the decrease in weight of the membrane was not significant.

The weight changes shown above are very small and may be due to experimental error or very slight

degradation of the polymer material. The change in the membrane properties may thus be due to a combination of very slight degradation of the membrane pores and ions lodging in the pores of the membrane. The Nafion 112E/H⁺ showed the highest weight loss in 0.1 M V(V) compared with the Gore Select membranes. The Nafion membrane also displayed the highest changes in resistivity and diffusivity after being soaked in the 0.1 M vanadium electrolyte for 120 days while the L-01009 membrane showed the lowest changes. Also, the diffusivity across the Nafion more than doubled while that for the L-01009 membrane remained fairly constant. The Gore Select L-01009 membrane had the best weight stability, but under certain conditions, especially when transferred from one solution to another of different composition, showed blistering on the surface of the membrane that could not always be reproduced.

The thickness of each of the membranes was also checked before and after soaking in the 0.1 M V(V) solution. The thickness of the membranes was measured using dial calipers after washing with distilled water and drying. The measured thickness of the membrane was taken as the average of five readings across different sections of the membrane. None of the membranes displayed a change in thickness. The low net weight loss and change in thickness could however, be due to the combined effect of polymer loss and vanadium fouling.

3.2. Chemical stability studies

Further experiments were conducted to determine the rate at which the membranes are degrading in the vanadium solutions. The membranes were soaked in 0.1 and 1 M V(V) solutions. As the membrane is oxidised by the V(V) species in solution, the yellow V(V) ions are reduced to blue V(IV) ions. These ions can be detected by UV-visible spectrophotometry which in turn gives an indication of the rate of membrane oxidation. As shown in Figures 2 and 3 the rate of deterioration varies with each membrane. In the 0.1 M V(V) solutions Nafion 112E/H⁺ shows the worst stability followed by the New Selemion membrane. A different trend is observed in the 1 M V(V) solutions, however. In the more concentrated solutions, the New Selemion displays the worst stability followed by the Porous Separator Gore P-01006 and then Nafion. The different concentration of ions present in each solution therefore has a significant effect on the membrane stabilities. Although the Nafion 112E/H⁺ membrane shows the greatest rate of initial deterioration, this levels off and remains stable. The New Selemion and Porous Separator are the least stable of the membranes in more concentrated vanadium solutions.

The results from the stability tests and performance after soaking in V(V) both indicate that the membranes degrade on exposure to the vanadium electrolytes, yet very little weight loss is observed when exposed to the electrolytes. The small observed weight loss of the

Table 3. Weight loss of membranes in 0.1 M V(V)

Membrane	Δ Weight /%
Nafion 112E/H ⁺	4.62
Gore Select L-790	1.62
Gore Select L-570	0.83
Gore Select L-01009	0.27

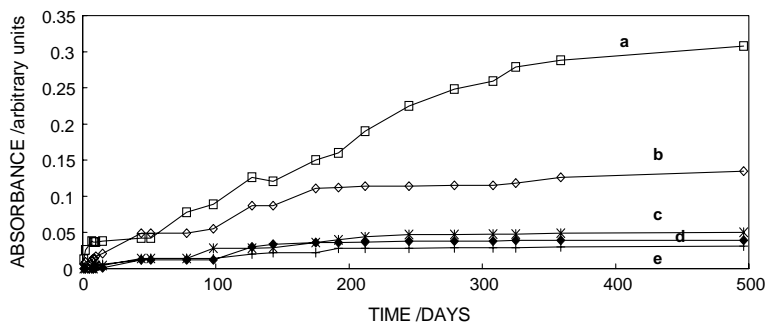


Fig. 2. Chemical stability of membranes soaked in the 0.1 M V(V) electrolyte. Curve a – Nafion 112E/H⁺; Curve b – New Selemion Type 3H; Curve c – Gore Select L-570; Curve d – Gore Select L-01009; Curve e – Porous separator P-01008.

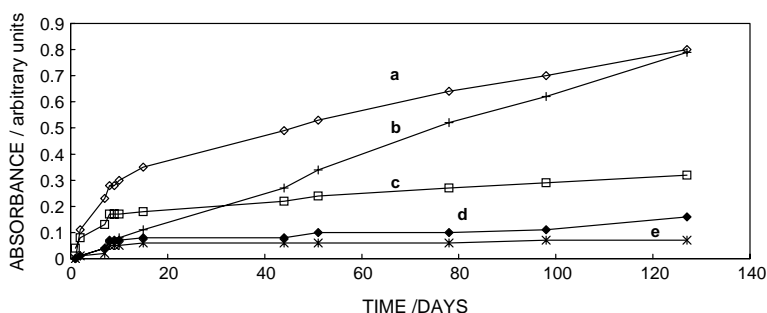


Fig. 3. Chemical stability of membranes soaked in the 1 M V(V) electrolyte. Curve a – New Selemion Type 3H; Curve b – Porous separator P-01008; Curve c – Nafion 112E/H⁺; Curve d – Gore Select L-01009; Curve e – Gore Select L-570.

membranes agrees however, with the concentration levels of V(IV) ions formed. As shown in Figure 2, an absorbance of 0.3 indicates a concentration of 0.02 mol/l V(IV) ions. A trend between the change in weight of the membranes and the concentration of V(IV) ions formed does exist. The membranes showing a higher formation of V(IV) ions (Figure 2) also show the larger changes in weight (Table 3).

Therefore, it is obvious that the oxidative V(V) ions cause the membranes to deteriorate and perform less efficiently in the vanadium battery. Of the membranes tested in the 0.1 M V(V) solution, The Nafion 112E/H⁺ showed the greatest loss in weight and also the greatest level of V(IV) ion formation in the absorbance experiments, while L-01009 displayed the smallest change in weight and the least amount of V(IV) ion formation. It is important to determine whether other ions in the solution are causing the membranes to foul and whether or not the damage is mainly physical. It is suspected that the pores of the membranes may be distorted in some way. This may be due to change in chemical composition of the pores or permanent enlarging of the pores by erosion or swelling.

After exposing the membranes to 0.1 M V(V) in 0.25 M H₂SO₄ solution for 60 and 120 days, FESEM analysis was used to determine if any changes had occurred during immersion. Images of the membrane pore structure could not be obtained however and this may have been due to the membranes being transparent to the FESEM beam or the beam is destroying the membranes. The membranes were also compared for

surface damage under an optical microscope, but no visible differences could be detected.

3.3. Cycling experiments

Cycling experiments were conducted to determine whether the membranes could maintain their performance in the vanadium battery for extended periods of time. The membranes were placed in a flow cell and exposed to continuous charge/discharge cycles. The overall coulombic, energy and voltage efficiencies of the cell were calculated. As shown in Figure 4, after 350 cycles the Gore Select L-570 membrane displayed an average coulombic efficiency of about 95% and average energy efficiency of about 80%. Figure 5 shows the results for the Gore Select L-01009 membrane. After about 1100 cycles this membrane displayed an average coulombic efficiency of 90%, an average voltage efficiency of about 85% and energy efficiency of 80%.

As shown in Figure 6 the capacity of the cell employing the Gore Select L-570 membrane fluctuated quite significantly and showed a significant decrease after 280 cycles. The L-570 membrane is therefore unable to maintain its capacity and performance in the vanadium battery. The capacity of the cell containing the Gore Select L-01009 membrane (Figure 7) shows better stability than the L-570 membrane, but starts to drop off after 400 cycles.

Both charts display large and small fluctuations. The larger fluctuations are due to the pumps stopping, cell leaking or topping up of the electrolyte solutions.

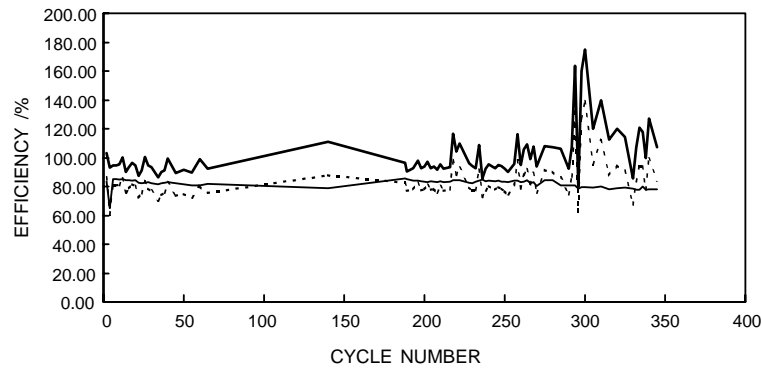


Fig. 4. Coulombic, energy and voltage efficiencies of vanadium cell employing Gore Select L-570 Membrane. (—) coulombic efficiency; (—) voltage efficiency; (- - -) energy efficiency.

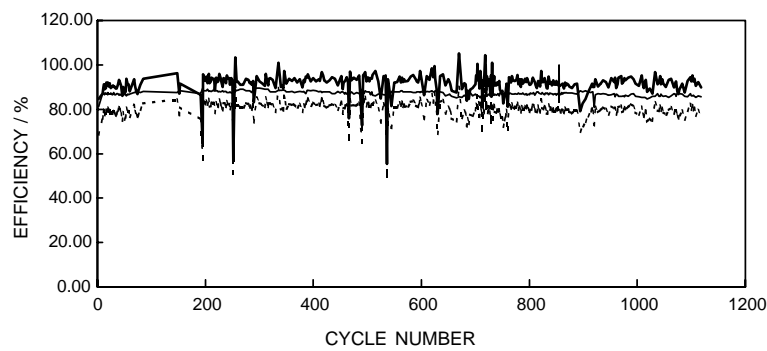


Fig. 5. Coulombic, energy and voltage efficiencies of vanadium cell employing Gore Select L-01009 Membrane. (—) coulombic efficiency; (—) voltage efficiency; (- - -) energy efficiency.

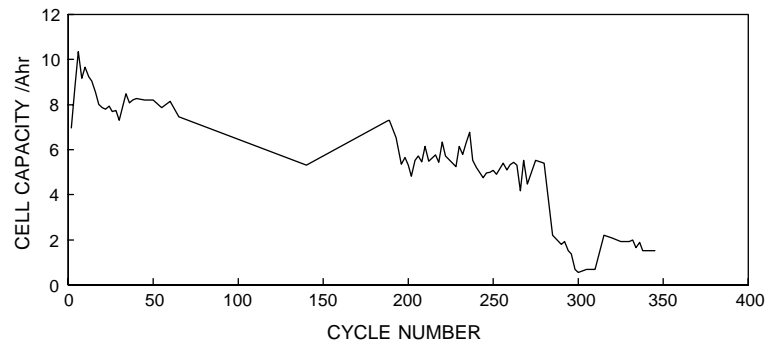


Fig. 6. Capacity vs cycle number for vanadium cell employing Gore Select L-570 membrane.

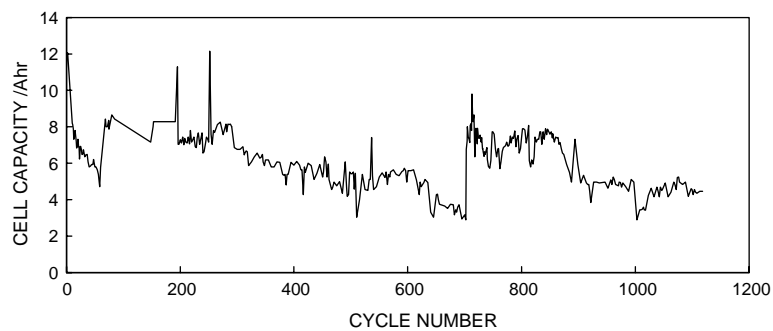


Fig. 7. Capacity vs cycle number for vanadium cell employing Gore Select L-01009 membrane.

Smaller fluctuations are due to a number of different causes. For example, preferential transport of vanadium ions from one half-cell to the other during cycling, will lead to a depletion of the vanadium content of one half-cell solution while the other becomes more concentrated. The bulk transfer of solution from one side to the other across the membrane also alters the capacity of the cell. In order to adjust the solutions for these changes and restore the cell's full capacity, therefore, the two half-cell solutions are re-mixed periodically, the frequency of which, depends on the membrane properties and cell operation.

The results obtained from the above experiments all show that the membranes are affected by the vanadium electrolyte, but the extent and rate of deterioration changes with vanadium ion concentration and total ionic strength of the solution. The dilute 0.1 M V(V) electrolyte appears to be entering the pores of the membranes more readily as the membranes swell significantly in this solution. The 0.1 M V(V) electrolyte thus causes accelerated deterioration of the membrane performance as a result of physical destruction, chemical modification or a combination of both. While this test solution provides useful information on the comparative behaviour of different membranes in diluted vanadium solutions, it should be stressed that this is not representative of an actual VRB electrolyte where the total vanadium ion concentration is between 1.6 and 2 M and the total sulphate concentration ranges from 4.4 to 5 M.

4. Conclusions

The selected membranes were found to have reasonable stability in the vanadium redox cell, although extended exposure to the fully charged positive half-cell solution did show a loss of membrane performance. The resistivity of the membranes was found to decrease after being soaked in 0.1 M V(V) in 0.25 M H₂SO₄ solution for extended periods of time. This may have been due to erosion of polymeric material. The IEC of the membranes was found to increase with soaking time. For example, the IEC of the Gore Select L-01009 increased from 1.2 to 2.0 after 60 days of soaking and further increased to 2.5 after 120 days. The increase in IEC might be attributed to anions (SO₄²⁻ and HSO₄⁻) from the solution lodging in the pores of the membrane. The V(IV) ion diffusivities of the membranes were also adversely affected on extended exposure to 0.1 M V(V) in 0.25 M H₂SO₄ solution. The faster rate of ion transfer could have contributed to the decrease in the resistance of the membrane.

Chemical stability tests were conducted to determine the rate at which the membranes degrade in the positive fully charged vanadium electrolyte. The results from the long-term stability tests indicate that the properties of membranes gradually deteriorate, although the degree of oxidation is low. This is supported by the fact that the membranes display little weight loss.

FESEM analysis could not detect any physical destruction to the membranes. This may be because the membranes are transparent to the beam. The Gore Select L-570 and L-01009 membranes displayed good stability in the vanadium flow cell charge-discharge cycling tests. While the results from the V(V) immersion tests showed considerable deterioration in the membrane selectivity, however, the membranes did not appear to show noticeable signs of deterioration in the flow cell. This is because the cell employs a more concentrated electrolyte with higher ionic strength, so that the degree of swelling is much lower than in the dilute solution. Furthermore, during continuous cycling in the cell, the membranes are not continually exposed to the oxidising V(V) ions, these being reduced to V(IV) during discharge. Also, the vanadium electrolyte is continually flowing past the membrane not allowing ions to precipitate or lodge in the pores during cycling. Any diffusion of vanadium ions into the pores of the membrane from each half-cell would lead to an oxidation-reduction reaction between the different oxidation states, producing V(III) and V(IV) ions in the pores. These ions are not oxidising like the V(V) species, so their effect on the membrane chemical stability will be much less than the V(V) solution. These ions may have different interaction with the fixed functional groups compared with the V(V) ions. While the results from the immersion tests provide useful comparative data on different types of candidate membrane materials for the vanadium redox flow cell, they do not predict the expected cycle life in an actual vanadium battery. This can only be obtained from long-term cycling experiments using different charge-discharge conditions appropriate for specific applications.

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